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Synthesis, Structures and Coordination Chemistry of Singly-Bridged Phosphane-Boranes with Coordinately Unsaturated Platinum Group Metals.

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A range of singly-bridged phosphane-boranes (PBs) have been investigated as potential ligands for basic transition metals. The PBs $Ph_2PC(Ph)=C(R)BR_2$ (R = Bu **1**, Ph **2**, Et **3**), based on a rigid *cis*-ethylene bridges, have been prepared, improving upon limited literature precedent. All three compounds have been comprehensively characterised for the first time, including by X-ray diffraction studies. Significant intramolecular P→B association is apparent in each case, which serves to preclude their engagement as ligands. In contrast, the more flexible PBs $R_2P(CH_2)_2BBN$ (R = Fu **5**, Ph **6**) readily coordinate to the platinum group metals Pt, Pd and Rh. These complexes have been fully characterised, including an X-ray diffraction study of $[Rh(CO)\{Fu_2P(CH_2)_2BBN\}_2Cl]$ (**13**).

Introduction

Amidst the currently resurgent activity in the chemistry of ambiphilic molecules, which possess both Lewis acidic and Lewis basic functionalities, of particular note and prominence are the phosphane-boranes (PBs). One recent impetus for this has been provided by the emergence of Stephan's Frustrated Lewis Pairs (FLPs),[1] their capacity for the ambient temperature, reversible activation of H_2 having been first identified with the PB $Mes_2P(C_6F_4)B(C_6F_5)_2$.[2] Subsequently, such species have found extensive utility in, *inter alia*, catalytic hydrogenation,[3] reversible binding of CO_2[4] and its reduction,[5] irreversible binding of N_2O,[6] ring-opening of cyclic ethers[7] and dehydration of ammonia-borane,[8] with a notable emphasis on PBs in which the ditopically active acid and base are proximally constrained.

Alongside these developments PBs feature prominently in the continuing development of the chemistry of 'metallaboratranes',[9] complexes in which buttressing donor functionalities support a transannular retrodative metal→boron bond. These compounds were first described by Hill,[10] as the result of intramolecular B–H activation of a coordinated hydrotris(methimazolyl)borate ligand, a synthetic route that was widely exploited and remains common.[11] Subsequently, Bourissou obtained related systems from basic metal salts and the *ortho*-phenylene bridged PBs $Ph_nB(o\text{-}C_6H_4PPh_2)_{3-n}$ (*n* = 0, 1),[12] thus providing more direct and targeted access. Metallaboratranes based on these PBs are now prominent, and have recently found utility in the catalytic cleavage of H_2[13,14] and the activation of silane Si–H bonds.[15]

Despite this activity, the coordination chemistry of 'simple' PBs that feature one donor and one acceptor function, separated by a single bridge, remains relatively underdeveloped, particularly with co-ordinately unsaturated metal centres. Thus, while Gröbe reported the synthesis of $[Rh\{P(Me_2)\{CMe\}_2BMe_2\}_2(CO)Cl]$,[16] no further coordination chemistry of this, or related ethylene-bridged PBs, has been described. In respect of PBs based on saturated linkers only a small amount of work exists, focussed on co-ordinately saturated metal centres. Thus, a decade after Braunschweig's report[17] of $[ML_n\{PMe_2CH_2BR_2\}]$ (R = NMe_2, ML_n = $Cr(CO)_5$, $Fe(CO)_4$, $Mn(CO)_2(\eta^5\text{-}C_5H_4Me)$; R = OMe, ML_n = $Cr(CO)_5$, $Fe(CO)_4$), the ruthenium complexes $[Ru(p\text{-cymene})\{PPh_2(CH_2)_2BR_2\}Cl_2]$ (BR_2 = BCy_2, 9-BBN) were described, and demonstrated to undergo borane-cleavage to afford metallacycles.[18] Recently, $[RuH(CO)\{PPh_2(CH_2)_2B(C_8H_{14})\}Cp]$ was reported,[19] along with an analogue containing the '$B(C_6F_5)_2$' fragment, which exhibits a borane-hydride interaction. The related PB $Mes_2P(CH_2)_2B(C_6F_5)_2$ has been shown to react with Cp_2ZrMe_2, effecting methide abstraction to afford the Zwitterionic $[Zr\{PMes_2(CH_2)_2B(C_6F_5)_2Me\}Cp_2Me]$;[20,21] similar behaviour was previously reported for $[Ni(dmpe)Me_2]$ with less acidic PBs, affording $[Ni(dmpe)\{PPh_2(CH_2)_2BR_2Me\}Me]$ (BR_2 = BCy_2, 9BBN).[22]

Bercaw has demonstrated Lewis-acid assisted reduction of a carbonyl moiety within $[Re(CO)_4\{PPh_2(CH_2)_nB(C_8H_{14})\}]BF_4$ (n = 1, 2, 3),[23] by virtue of the pendant borane functionality, which facilitates hydride transfer and can also assist in H_2 activation as the acidic component of an intermolecular FLP.[24] A key feature in both instances is the capacity of the pendant borane to stabilise the resulting formyl moiety (via O→B association); this has also been described more recently with diphosphanyl(organyl)boranes in the complexes $[M(CO)_4\{\kappa^2\text{-}P,P\text{-}(PPh_2)_2CH_2B(C_8H_{14})\}Br]$ and $[M(CO)_4\{\kappa^2\text{-}P,P\text{-}(Ph_2P)CH(PPh_2)CH_2B(C_8H_{14})\}Br]$ (M = Mn, Re).[25] These ligands have also been employed in a series of group 6 nitrosyl complexes, in which the borane remains pendant.[26]

We have an interest in extending the coordination chemistry of 'simple' PBs, with a view to either accessing examples of hitherto unrealised singly-buttressed metal→boron linkages or, through their frustration, establishing cooperativity between the borane and a basic metal centre. To this end, we have had cause to revisit PBs of the type $Ph_2PC(Ph)=C(R)BR_2$ and $R'_2P(CH_2)_nB(C_8H_{14})$. Herein we describe the solid state structures of $Ph_2PC(Ph)=CRBR_2$ (R =

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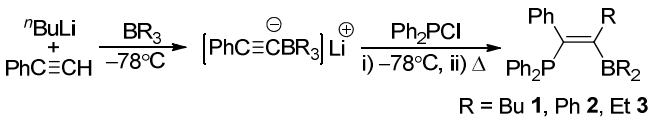
Ph, *n*-Bu) and synthesis of the PB $Fu_2P(CH_2)_2B(C_8H_{14})$. The coordination chemistry of the latter, and its analogue $Ph_2P(CH_2)_2B(C_8H_{14})$, is described, including isolation of the first co-ordinately unsaturated complexes of any such ligand; the solid-state structure of the complex $[Rh(CO)\{Fu_2P(CH_2)_2B(C_8H_{14})\}_2Cl]$ is also reported.

Results and Discussion

Synthesis and characterisation of ethylene-bridged PBs.

A common feature of known metal-borane complexes is the presence of a geometrically constrained two-atom bridge between the donor and acceptor functionalities; it is equally apparent that relatively modest acidity is adequate to facilitate an M → B interaction. We thus reasoned that while such interactions are absent from Gröbe's $[Rh\{P(Me_2)\{CMe\}_2BMe_2\}_2(CO)Cl]$,[16] perhaps reflecting a need for two supporting buttresses, complexes of this type must, nonetheless, retain appreciable acidity/basicity that might reasonably be exploited.[27] To this end, we sought initially to further investigate ethylene-bridged PBs embodying appreciable steric encumbrance, with modest acidity at boron.

The PBs $Ph_2PC(Ph)=C(R)BR_2$ (R = Bu **1**, Ph **2**, Et **3**) were obtained in a one-pot procedure, following from Binger's methodology.[28] Thus, the alkynylborates $Li[R_3BC{\equiv}CPh]$ were prepared, *in situ*, from the respective boranes and LiC≡CPh, then treated with Ph_2PCl (Scheme 1). After several hours at reflux (**1** and **2**) concentration of the resulting solutions and storage at –80°C allowed for isolation of the products in modest yield (~30 %) as crystalline solids. In the case of **3**, the final reaction step must be performed at ambient temperature, reflux seemingly inducing loss of the borane to afford appreciable quantities of $Ph_2PC{\equiv}CPh$; this has previously been described as a major contaminant (ca 20 %) in the synthesis of **1**,[29] however, we find this can be diminished in all cases by performing all reagent additions at −78 °C.



Scheme 1. Synthesis of $Ph_2PC(Ph)=C(R)BR_2$ (R = Bu **1**, Ph **2**, Et **3**).

While both **1**[29] and **2** [16b,30] have been previously described, few substantive characterising data were reported. All three compounds exhibit $^{11}B\{^1H\}$-NMR chemical shifts characteristic of 4-coordinate boron (δ_B **1** 13.5, **2** 4.1, **3** 13.2), consistent with the presence of a P→B interaction, a feature that is supported by the appreciably higher frequency of the $^{31}P\{^1H\}$ NMR resonances (δ_P **1** 10.0, **2** 7.4, **3** 9.8)[31] when compared to $Ph_2PC{\equiv}CPh$ (δ_P –34),[29] $Ph_2PCH{=}CH_2$ (δ_P –10.7),[32] and $MeCH{=}CHPPh_2$ (δ_P *cis* –32.7, *trans* –14.2).[33] The ancillary organic moieties are apparent from the ^1H-NMR spectra, the integrations of which are consistent with both identity and purity, and from the $^{13}C\{^1H\}$ NMR spectra, in which the alkene backbone is clearly apparent (δ_C 126.5, 195.2 **1**; 128.0, 181.3 **2**; 126.4, 196.0 **3**). Ultimately, the identities of all three compounds were unequivocally established from X-ray diffraction studies (Figure 1, Table 2); though the data for **3** are of low quality, they do confirm connectivity comparable to that of **1** and **2**.

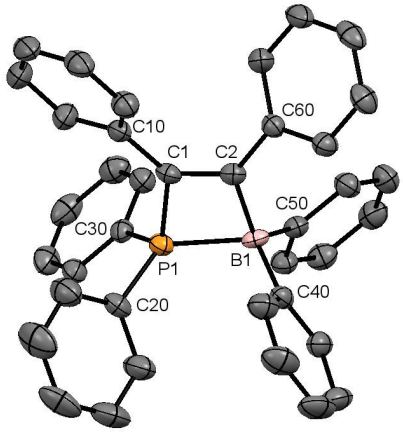


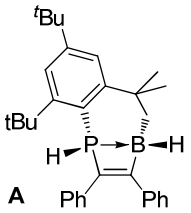
Figure 1. Molecular geometry of compound **2** (50 % thermal ellipsoids) with hydrogen atoms omitted for clarity. The core 1-borata-4-phosphinio-cyclobu-2-ene unit labelling is directly transposable to compounds **1** and **3**, see SI for full details and plots.

Table 1. Selected bond distances [Å] and angles [°] for **1** and **2**, with estimated standard uncertainties in parentheses.

	1	**2**	**3**[a]
P1–B1	2.107(2)	2.002(2)	2.077(5)
P1–C1	1.799(2)	1.797(2)	1.797(4)
C1–C2	1.361(3)	1.363(3)	1.385(6)
C2–B1	1.630(3)	1.659(3)	1.634(8)
P1–B1–C2	77.82(12)	80.31(12)	78.5(3)
P1–C1–C2	96.51(14)	96.53(15)	95.6(3)
P1–C1–C10	131.61(15)	130.44(16)	131.9(3)
C1–P1–B1	76.59(10)	78.25(9)	77.7(2)
C1–C2–B1	108.50(17)	104.90(17)	107.5(4)
B1–C2–C60	124.91(18)	128.74(18)	127.8(5)

[a] Data for **3** are shown for geometric comparison only, the structure has two molecules in the asymmetric unit which exhibit significant disorder, precluding meaningful analysis of bond distances/angles.

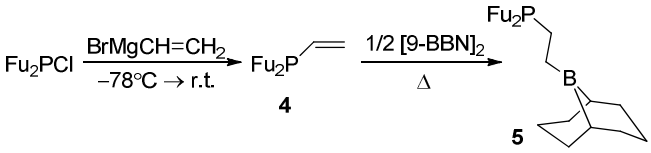
All three compounds adopt the anticipated 1-borata-4-phosphino-cyclobut-2-ene geometry, with a significant P → B interaction, which is most pronounced within **2** (2.002(2) Å), as is also apparent from the ^{11}B NMR data (*vide supra*). Indeed, this is one of the shortest P→B interactions yet observed within such a geometric motif, second only to that within Stephan's constrained, bicyclic **A** (1.993(16) Å).[34] The distance in **2** is also notably shorter than is usual for acyclic adducts of the type $Ph_2RP\rightarrow B(C_6F_5)_2R$, which typically lie in the range 2.03 – 2.18 Å.[35] The enhanced P→B interaction of **2** results in a notable contraction of the B–C=C angle (104.90(17) °) relative to that in **1** (108.50(17) °), with concomitant increase of the angles about boron (∠ 80.31(12) ° **2**, 77.85(12) ° **1**) and phosphorus (∠ 78.25(9) ° **2**, 76.59(10) ° **1**); the internal geometries are otherwise unremarkable, being consistent with other similarly constrained heterocycles.



Following from Gröbe's report of $Me_2PC(Me)=C(Me)BMe_2$,[16] we sought to effect the coordination of **1** – **3** to a range of late transition metal centres (e.g. $[RhL_2Cl]_2$, $L_2 = (CO)_2$, η^4-C_8H_{12}; ML_2Cl_2, M = Pt, Pd, $L_2 = (NCPh)_2$, η^4-C_8H_{12}). Unfortunately, this proved unsuccessful, typically resulting in either recovery of the unchanged PB, or its degradation to intractable species.

Synthesis and coordination chemistry of 'flexible' PBs.

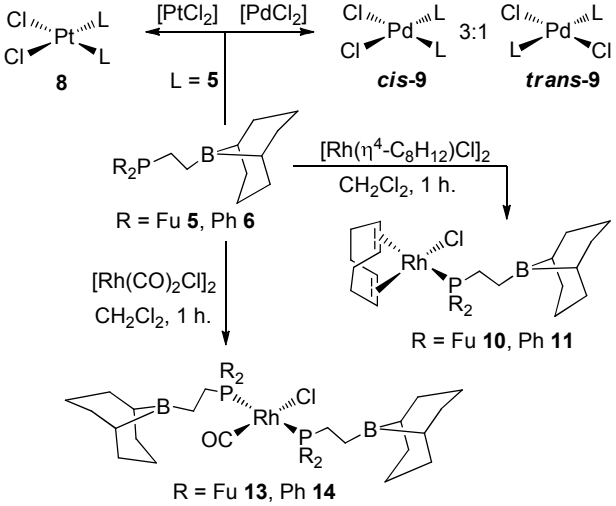
The bis(2-furanyl)vinyl phosphane $Fu_2PCH=CH_2$ (**4**, Scheme 2) was prepared in high yield (> 80 %) from Fu_2PCl and $BrMgCH=CH_2$, its identity being established spectroscopically. The ^1H NMR spectrum exhibits a characteristic pattern of vinylic resonances consistent with the ABMX spin system, while a single $^{31}P\{^1H\}$ NMR resonance is observed (δ_P –57.1); bulk purity was affirmed by microanalysis. The subsequent hydroboration of **4** with the 9-BBN dimer proceeds over 3 h. at 60°C in toluene to afford $Fu_2P(CH_2)_2B(C_8H_{14})$ (**5**), which exhibits spectroscopic data consistent with those reported for the similarly obtained $Ph_2P(CH_2)_2B(C_8H_{14})$ (**6**).[18] In particular, only marginal change in the chemical shift of the phosphorus centre (δ_P –56.0) alongside an ^{11}B shift consistent with 3-coordinate boron (δ_B 87.7) conclusively demonstrate adoption of an 'open' geometry, devoid of the P→B interactions that have been noted for the more flexible $Ph_2P(CH_2)_3B(C_8H_{14})$ (**7**).[36]



Scheme 2. Synthesis of bis(2-furanyl)vinylphosphane and its hydroboration to the phosphane-borane **5**.

All three PBs **5** – **7** were investigated as ligands toward a range of late transition metals, with markedly varying results. Thus, **5** reacts cleanly with ½ equivalent of either $PtCl_2$ or $PdCl_2$ in dichloromethane, to afford the respective $[M(\mathbf{5})_2Cl_2]$ (M = Pt **8**, Pd **9**, Scheme 3). Spectroscopic data indicate the exclusive formation of ***cis*-8** (δ_P –17.5, J_{PtP} 3690 Hz), while **9** is obtained as a 3:1 mixture of *cis* and *trans* isomers (δ_P 0.89 and –11.4 respectively). Assignment of the *trans* isomer follows from both the established trend in δ_P for *cis*/*trans* isomers (i.e. $\delta_{Pcis} > \delta_{Ptrans}$[37]) and the manifestation of virtual coupling in the ^1H and $^{13}C\{^1H\}$ NMR data for the 2-furanyl moiety;[38] the ^1H-NMR chemical shifts of these moieties also compare well with related systems (*vide infra*) while those of the *cis* isomer agree well with data for **8**.[39,40]

In contrast to **5**, for neither **6** nor **7** were viable complexes obtained with either palladium or platinum, the free PBs typically being lost to intractable reaction mixtures. However, somewhat greater success was achieved with rhodium(I) precursors, both **5** and **6** smoothly cleaving the dimer $[Rh(\eta^4\text{-}C_8H_{12})Cl]_2$ to afford $[Rh(\eta^4\text{-}C_8H_{12})(L)Cl]$ ($L = R_2P(CH_2)_2B(C_8H_{14})$, R = Fu **10**, Ph **11**) in high yield, as evidenced by appreciably shifted (+Δδ) $^{31}P\{^1H\}$ NMR resonances with attendant coupling to rhodium (δ_P 2.8 J_{RhP} 155 Hz, **10**; 28.9 J_{RhP} 147 Hz, **11**). In each case, retention of the cyclooctadiene ligand and ancillary phosphane substituents was confirmed by ^1H and $^{13}C\{^1H\}$ NMR data, the borane being apparent from a characteristic resonance (δ_B 85.4 **10**, 81.5 **11**) that is only modestly perturbed from the free ligands. Notably, **7** also reacts in a similar fashion to afford $[Rh(\eta^4\text{-}C_8H_{12})\{PPh_2(CH_2)_3B(C_8H_{14})\}Cl]$ (**12**: δ_P 26.1 J_{RhP} 147 Hz) in which the borane moiety again remains pendant (δ_B 87.3) despite the greater flexibility within this ligand.



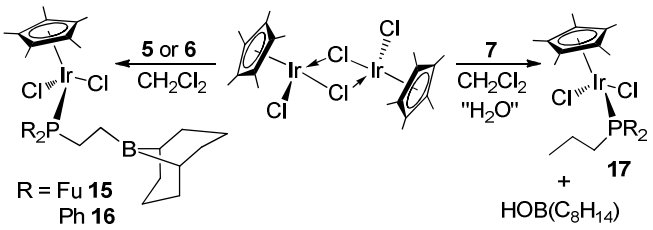
Scheme 3. Coordination chemistry of ligands **5** and **6**.

Both **5** and **6** were also found to cleave the rhodium chlorocarbonyl dimer $[Rh(CO)_2Cl]_2$ to afford $[Rh(CO)(L)_2Cl]$ ($L = R_2P(CH_2)_2B(C_8H_{14})$, R = Fu **13**, Ph **14**). Once again, ligation of the PBs and retention of a 3-coordinate boron centre were apparent from spectroscopic data (δ_P –5.59 (J_{RhP} 129 Hz) **13**, 29.0 (J_{RhP} 127.5 Hz) **14**; δ_B 85.9 **13**, 84.5 **14**), while assignment of a *trans* geometry at the metal followed from the manifestation of virtual coupling within the P-bound hydrocarbon moieties. Both complexes exhibit a single carbonyl stretching mode, consistent with the 'Rh(CO)Cl' moiety (ν_{CO} 1994 cm^{-1} **13**; 1966 cm^{-1} **14**); these also serve to illustrate the significantly reduced basicity of **5** compared with its diphenyl analogue. Indeed, complex **13** is only the third chlorocarbonylrhodium species to incorporate a phosphane ligand bearing the 2-furanyl moiety, after $[Rh(CO)\{PPh_2(Fu\text{-}SEt\text{-}5)\}Cl_2]$ and $[Rh(CO)\{PPh_2(Fu\text{-}SEt\text{-}5)\}_2Cl]$ (ν_{CO} 1990 cm^{-1} and 1982 cm^{-1} respectively).[41] The most closely comparable system, from a basicity point of view, would seem to be $[Rh(CO)\{PPh_2(N\text{-pyrrole})\}_2Cl]$ (ν_{CO} 1993 cm^{-1}),[42] while analogues with the $PPh(N\text{-pyrrole})_2$ (ν_{CO} 2007 cm^{-1}), $P(N\text{-pyrrole})_3$ (ν_{CO} 2024 cm^{-1}),[42] and $P(C_6F_5)_3$ (ν_{CO} 2003 cm^{-1})[43] ligands exhibit further reduced back-donation to the carbonyl.

X-ray quality single crystals of **13** were obtained by the slow-evaporation of a dichloromethane solution, the diffraction study (Figure 2) confirming the anticipated geometry about rhodium with inter-ligand angles in the range 89.9 – 90.1°. The ligated PBs each assume an anti-configuration at the C_2H_4 bridge, with the "P-CH_2" linkages lying coplanar with the $Rh(CO)(P)_2Cl$ unit. Consequently, the borane functions assume distal positions and remain pendant, with no discernible intra- or intermolecular associations with either the metal centre or ancillary ligands. Indeed, association of the

borane moiety with ancillary ligands is rare among the limited range of such complexes reported to date, though was recently noted within [RuH(CO){$PPh_2(CH_2)_2BR_2$}Cp'] (BR_2 = 9-BNN, $B(C_6F_5)_2$; Cp' = Cp, Cp*), which exhibit bridging hydrides (Ru–H–B), while a Ru–Cl–B interaction was inferred upon hydride exchange with CH_2Cl_2 (where BR_2 = 9-BBN).[19] Moreover, both Bercaw[23,24] and Berke[25] note association of the pendant borane with a formyl unit upon reduction of a carbonyl ligand within $[Re(CO)_4\{PPh_2(CH_2)_nB(C_8H_{14})\}]BF_4$ and $[M(CO)_4\{\kappa^2\text{-}P,P\text{-}(PPh_2)_2CH_2B(C_8H_{14})\}Br]$ respectively, but not with the terminal carbonyls themselves. It thus seems likely that the ethyl bridge affords inadequate flexibility to facilitate interaction with a *cis*-disposed ligand, without at least modest contraction of the *cis*-interligand angle.

fortuitous isolation of X-ray quality crystals, revealed to be the diphenylpropylphosphane complex **17** (Figure 3).



Scheme 4. Reactivity of **5**, **6** and **7** toward $[Cp^*IrCl_2]_2$.

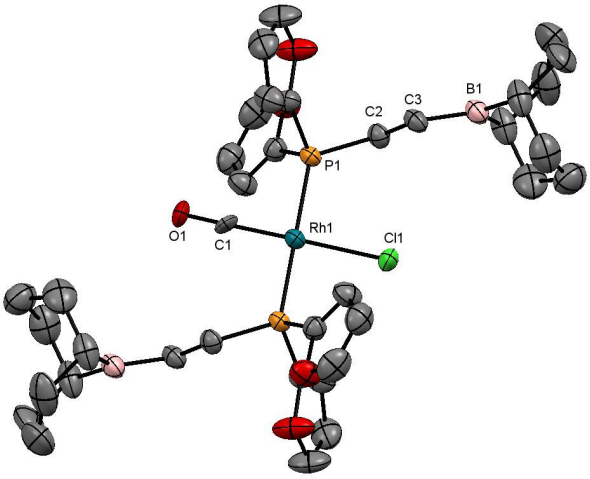


Figure 2. Molecular structure of **13** (50 % thermal ellipsoids), with hydrogen atoms omitted for clarity. The carbonyl and chloride ligands are both refined across two equivalent positions (50 % occupancy), such that the rhodium atom sits on an inversion centre; equivalent atoms are generated by symmetry transformation (–x + 1, –y +1, –z + 1). Selected bond distances [Å] and angles [°]: Rh(1)–Cl(1) 2.378(6), Rh(1)–C(1) 1.750(18), C(1)–O(1) 1.16(2), Rh(1)–P(1) 2.3114(10), P(2)–Rh(1)–Cl(3) 91.16(9), P(2)–Rh(1)–C(5) 89.9(5)

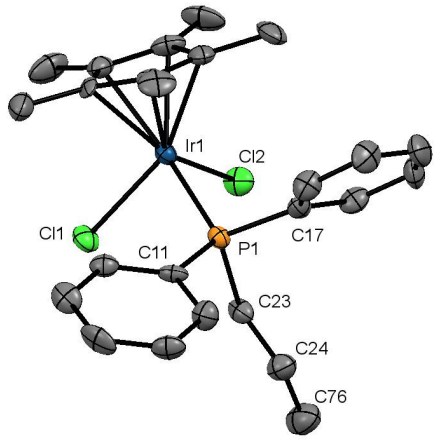


Figure 3. Molecular structure of **17** (50 % thermal ellipsoids), with hydrogen atoms omitted for clarity. The asymmetric unit comprises two molecules with comparable geometry, see SI for full plots Selected bond distances [Å] and angles [°]: Ir(1)–Cl(1) 2.415(2), Ir(1)–Cl(2) 2.411(2), Ir(1)–P(1) 2.308(2), P(1)–C(11) 1.831(7), P(1)–C(17) 1.827(7), P(1)–C(23) 1.825(7), C(23)–C(24) 1.508(10), C(24)–C(76) 1.519(11), Cl(1)–Ir(1)–Cl(2) 90.51(6), Cl(1)–Ir(1)–P(1) 87.42(6), Cl(2)–Ir(1)–P(1) 88.39(7), C(11)–P(1)–C(17) 105.5(3), C(11)–P(1)–C(23) 1003.5(3), C(17)–P(1)–C(23) 105.0(3), P(1)–C(23)–C(24) 119.1(5), C(23)–C(24)–C(76) 111.3(6).

The Ir(III) dimer $[IrCl_2Cp^*]_2$ was also found to react smoothly with both **5** and **6**, effecting near quantitative conversion to $[Ir\{PR_2(CH_2)_2B(C_8H_{14})\}Cl_2Cp^*]$ (R = Fu **15**, Ph **16**; Scheme 4). Both complexes again exhibit 3-coordinate boron centres (δ_B 87.8 **15**, 87.0 **16**), indicating an absence of any M→B or M–Cl→B interactions. While this is consistent with the situation described for the geometrically related Ru(II) complexes [Ru(*p*-cymene){$PPh_2(CH_2)_2BR_2$}Cl_2] (BR_2 = BCy_2, 9-BBN),[18] both differ markedly from the more recently described [Ru(CO){$PPh_2(CH_2)_2B(C_8H_{14})$}ClCp], for which an appreciable Ru–Cl→B interaction is noted.[19] The lack of such interaction within **15** or **16** presumably reflects the reduced basicity of Ir(III) compared with Ru(II).

The comparable reaction between $[IrCl_2Cp^*]_2$ and the more flexible PB **7** is less facile, and fails to result in a single clean product. In addition to unconsumed **7**, the $^{11}B\{^1H\}$ spectrum indicates the presence of two species in the 3-coordinate region (δ_B 88.0, 58.9), while the $^{31}P\{^1H\}$ NMR spectrum exhibits multiple species, dominated by resonances at –3.2 and –3.5 (3:2), which remain unassigned. A modest resonance 36.7 ppm is consistent with metal-coordination of the phosphorus centre. Attempts to separate this mixture by fractional crystallisation resulted in the

The generation of the coordinated Ph_2P^nPr ligand from **7** has precedent, $[Pd\{PPh_2(CH_2)_2CH_3\}Cl_2]_2$ having been isolated upon the hydrolysis of $[Pd(\mathbf{7})Cl_2]_2$.[44] The formation of **17** can thus reasonably be attributed to adventitious water. That hydrolysis occurred during synthesis, rather than recrystallisation, can be reconciled with spectroscopic data; the $^{11}B\{^1H\}$ NMR resonance at 58.9 ppm is consistent with the hydrolysis by-product $HOB(C_8H_{14})$ (δ_B ~ 57),[45] the associated hydroxyl ^1H resonance of which is also apparent (δ_H 5.54 *cf.* 5.58 lit[45]), albeit at trace levels given the prevalence of resonances associated with the BBN and phenyl fragments. Somewhat surprisingly, we also encountered hydrolytic ligand cleavage in the reaction of **6** with $[Ir(C_8H_{12})Cl]_2$; in this instance, apparently quantitatively. Thus, spectroscopic data indicate a single phosphorus-containing product (δ_P 17.7, *cf.* –10.1 for free **6**), and a single, 3-coordinate boron centre (δ_B 57.9). The latter is again consistent with $HOB(C_8H_{14})$, the associated hydroxyl proton of which is clearly observed (δ_H 5.58). The prevalence of these side-reactions is puzzling, given that they cannot be attributed to any single variable with respect to either reagents or protocol. We have thus been unable to establish the source of

adventitious water, though have noted the same outcome during subsequent synthetic attempts.

Conclusions

We have described the improved synthesis, and first comprehensive characterisation of the ethylene-bridged phosphane-boranes $Ph_2PC(Ph)=C(R)BR_2$ (R = Bu **1**, Ph **2**, Et **3**). Crystallographic and spectroscopic data demonstrate the adoption intra-molecular 'closed' structures, that of **2** involving one of the strongest such P→B interactions yet observed; however, these features render **1** – **3** ineffective for metal-ligation. In contrast, a range of late transition metal complexes of the new PB $Fu_2P(CH_2)_2B(C_8H_{14})$ (**5**), and its precedent analogue $Ph_2P(CH_2)_2B(C_8H_{14})$ (**6**), have been obtained, many involving co-ordinately unsaturated metal centres. Universally, the ligands exhibit pendant borane functionalities with no evidence for even marginal interaction with the metal centres or ancillary ligands. For *trans*-$[Rh(CO)\{Fu_2P(CH_2)_2B(C_8H_{14})\}_2Cl]$, this was confirmed crystallographically, the boranes assuming distal positions about the metal centre.

Experimental Section

General Information: All manipulations were performed under anaerobic conditions using standard Schlenk line and glovebox techniques, under an atmosphere of dry Argon or dinitrogen respectively. Solvents were distilled from appropriate drying agent and stored over either 4 Å molecular sieves (DCM and THF) or potassium mirrors (non-halogenated). All reagents were obtained from either Sigma-Aldrich or Fisher; precious metal salts were obtained from STREM. NMR spectra were recorded on a Varian VNMRS 400 MHz spectrometer (^{1}H 399.5 MHz, ^{13}C 100.46 MHz, ^{31}P 161.71 MHz, ^{11}B 128.17 MHz, ^{195}Pt 85.59 MHz) and referenced to external Me_4Si, 85 % H_3PO_4, BF_3.OEt or K_2PtCl_6 as appropriate. Carbon-13 assignments were verified by recourse to 2D (HSQC, HMBC) spectra. All data were recorded at 303 K unless otherwise stated. Mass spectrometric data were recorded by Dr A.-A. Sada of the departmental service; microanalyses were performed by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.[46]

Crystal Structure Determination: The data collection and structure refinement data for compounds **1**, **2**, **3**, **13** and **17** are shown in Table 2. Data were collected on either an Enraf-Nonius CAD4 with κ-CCD area detector using Mo-Kα radiation (λ = 0.71073), or an Agilent Xcalibur Eos Gemini Ultra with CCD plate detector using Cu-Kα radiation (λ =1.54184). Structure solution and refinement were performed using SHELXS[47] and SHELXL[47] respectively, running under WinGX[48] or Olex2.[49] CCDC-1013335 (**1**) 1013336 (**2**) 1013337 (**13**) and 1013338 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $Bu_2BC(Bu)=C(Ph)PPh_2$ (1): To a cold (−78°C) solution of phenylacetylene (0.73 g, 7.19 mmol) in Et_2O (6 cm^3) was added, drop-wise, *n*-BuLi (2.9 cm^3, 2.5 M, 7.2 mmol). The resulting colourless mixture was allowed to stir for 1 h. at −78 °C then an ethereal solution of tributyl-borane (7.2 cm^3, 1 M, 7.2 mmol) was added drop-wise. The mixture was allowed to warm slowly to ambient temperature over 1.5 h. with continued stirring, before the drop-wise addition of Ph_2PCl (1.58 g, 7.2 mmol) as solution in Et_2O (1.5 cm^3), resulting in the immediate emergence of a white precipitate. The resulting mixture was heated to reflex for 3 h.. After allowing to cool, the solution was filtered to remove LiCl and the filtrate concentrated under reduced pressure. Storage at −80°C for 48 h. resulted in formation of a white solid, which was isolated by filtration, washed with cold pentane and dried in vacuo as a microcrystalline powder. Yield 1.02 g, 30.2 %. ^{1}H-NMR ($CDCl_3$): δ_H 0.73 (t, 6H, J = 6.65 Hz, 2 x B-$(CH_2)_3CH_3$), 0.82 (m, 4H, 2 x BCH_2), 0.89 (t, 3H, J = 7.71 Hz, $(CH_3)_3CH_3$), 1.16 (br, 6H, 'CH_2'), 1.33 (m, 2H, $(CH_3)_2CH_2CH_3$), 1.52 (m, 4H, 2 x B$(CH_2)_2CH_2$), 2.5 (m, 2H, CCH_2), 7.13-7.26 (m, 5H, Ar-C**H**), 7.34-7.49 (m, 10H, PAr-C**H**). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 14.1 (s, CH_3), 14.2 (s, $B(CH_2)_3CH_3$), 23.5 (br, $(CH_2)_2CH_2$), 26.6 (s, $B(CH_2)CH_2$), 30.4 (d, $J_{C\text{-}P}$ = 10.6 Hz, $(CH_2)CH_2$), 30.7 (d, $J_{C\text{-}P}$ = 2.08 Hz, $B(CH_2)_2CH_2$), 34.3 (d, J_{CP} 46.7 Hz, C=C(CH_2)) 126.5 (s, =C(BR_2)), 126.8 (s, Ar), 128.4 (s, Ar), 128.6 (d, $J_{C\text{-}P}$ = 3.38 Hz, PPh), 128.6 (d, $J_{C\text{-}P}$ = 8.46 Hz, PPh), 130.1 (d, $J_{C\text{-}P}$ = 2.23 Hz, PPh), 131.6 (d, $J_{P\text{-}C}$ = 17.36 Hz, i-C**H**), 132.9 (d, $J_{C\text{-}P}$ = 11.04 Hz, PPh), 136.9 (d, $J_{C\text{-}P}$ = 1.89 Hz, Ar), 195.2 (d, J_{CP} 83 Hz, P**C**=). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P 10.0 (s, **P**Ph_2). ^{11}B{^{1}H} NMR ($CDCl_3$, 303K): δ_B 13.9 (s, **B**Bu_2). EI-MS: *m/z*: 468 [M]$^+$. Elem. Anal.: Calcd for $C_{32}H_{42}BP$: C, 82.04 %; H, 9.04 %. Found; C, 81.95 %; H, 9.17 %. ***Crystal data for 1***: $C_{32}H_{42}BP$, M_w=468.44, Monoclinic, P21/c (no. 14), a = 9.1875(7), b = 29.734(2), c=10.5528(9) Å, α = 90, β = 94.933(2), γ = 90°. V= 2872.2(4) A^3, Z = 4, D_c 1.083 Mg/m^3. μ(Mo-Ka) = 0.113 mm^{-1}, T = 173(2) K, 6120 independent reflections. Full-matrix F^2 refinement R_1 = 0.0588, wR_2 = 0.1605 on 4371 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 55 °], .307 parameters. CCDC 1013335

Synthesis of $Ph_2BC(Ph)=C(Ph)PPh_2$ (2): In a similar fashion to **1**, the lithiation of phenylacetylene (0.6 g, 5 mmol) in Et_2O (2 cm^3) at −78 °C was followed, after 1 h., by the addition of Ph_3B (1.22 g, 5.03 mmol) as solution in Et_2O (15 cm^3), which was accompanied by a yellow colouration, which discharged with stirring. Having attained ambient temperature over 1.5 h., Ph_2PCl (0.82 g, 4.6 mmol) in Et_2O (2 cm^3) was added, then the mixture brought to reflux for 3 h. After allowing to attain ambient temperature, the mixture was concentrated in vacuo, resulting in precipitation of **2** alongside the LiCl by-product. The solid was isolated by filtration, then the product extracted into dichloromethane. Storage of the concentrated CH_2Cl_2 solution at −80°C for 48 h. afforded **2** as a white solid that was isolated by filtration and dried *in vacuo*. Yield: 0.80 g, 30.3 %. ^{1}H NMR (CD_2Cl_2): δ_H 7.12 (m, 6H, Ar-**H**), 7.16-7.28 (m, 16H, Ar-**H**), 7.33-7.39 (m, 6H, Ar-**H**), 7.42 (t, 2H, $^2J_{H\text{-}H}$ = 6.76 Hz). ^{13}C NMR (CD_2Cl_2): δ_C 126.0 (d, $J_{C\text{-}P}$ = 4.00 Hz, PAr), 127.5 (d, $J_{C\text{-}P}$ = 2.74 Hz, PAr), 128.0 (s =C(BR_2)), 128.1 (s, Ar), 128.29 (s, Ar), 128.5 (s, Ar), 128.5 (s, Ar), 128.6 (d, $J_{C\text{-}P}$ = 4.05 Hz, PAr), 128.9 (d, $J_{C\text{-}P}$ = 10.01 Hz, PAr), 129.1 (s, Ar), 140.0 (d, $J_{C\text{-}P}$ = 1.2 Hz, PAr), 131.2 (d, $J_{C\text{-}P}$ = 3.5 Hz, PAr), 132.6 (s, Ar), 133.0 (s, Ar), 133.5 (d, $J_{C\text{-}P}$ = 9.39 Hz, PAr), 136.2 (d, $J_{C\text{-}P}$ = 9.3 Hz, PAr), 136.8 (d, br, $J_{C\text{-}P}$ = 2.57 Hz, PAr), 140.5 (s), 140.9 (s), 181.3 (br. m., P**C**=). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_P 7.48 (s, **P**Ph_2). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ_B 4.08 (s, **B**Ph_2). EI-MS: m/z = 528 [M]$^+$. ***Crystal data for 2***: $C_{38}H_{30}BP$, M_w=528.40, triclinic, P-1 (no. 2), a = 10.3576(3), b = 11.1069(5), c = 14.6458(3) Å, α = 107.201(2), β = 90.840(2), γ = 112.862(4)°. V = 1466.92(10) A^3, Z = 2, D_c 1.196 Mg/m^3. μ(Cu-Ka) = 1.003 mm^{-1}, T = 173(2) K, 5495 independent reflections. Full-matrix F^2 refinement R_1 = 0.0624, wR_2 = 0.2135 on 4984 independent absorption corrected reflections. [$I > 2\sigma(I)$; $2\theta_{max}$ = 140.4 °], 361 parameters. CCDC 1013336

Synthesis of $Et_2BC(Et)=C(Ph)PPh_2$ (3): Similarly to **1** and **2**, to an ethereal solution (5 cm^3) of lithiated phenylacetylene (0.79 g, 7.19 mmol) at −78 °C was added Et_3B (3.6 cm^3, 2 M in Et_2O, 7.2 mmol). The mixture was maintained at −78 °C while stirring for 1.5 h., before the dropwise addition of Ph_2PCl (1.58 g, 7.2 mmol) as solution in Et_2O (2 cm^3). The resulting mixture was allowed to attain ambient temperature and then

stirred for 4 h. The mixture was then filtered to remove LiCl and the filtrate taken to dryness under reduced pressure to afford an oil, which spontaneously crystallises on standing. Yield: 1.78 g, 64 %. ^{1}H NMR ($CDCl_3$): δ_H 0.79 (m, 6H, BCH_2CH_3), 0.86 (m, 4H, BCH_2), 1.11 (t, 3H, $^3J_{H-H}$ = 7.66 Hz, CCH_2CH_3), 2.55 (qd, 2H, $^3J_{H-H}$ = 7.65 Hz, $^4J_{H-P}$ = 2.96 Hz, C=C-CH_2), 7.13 (m, 1H, CAr-CH), 7.19 (m, 1H, CAr-CH), 7.23 (m, 2H, PAr-CH), 7.36 (m, 2H, PAr-CH), 7.41 (m, 2H, PAr-CH), 7.42 (m, 2H, PAr-CH). ^{13}C NMR ($CDCl_3$): δ_C 11.5 (d, $^4J_{C-P}$ = 11.6 Hz, BCH_2CH_3), 13.2 (d, $^3J_{C-P}$ = 2.89 Hz, CH_2CH_3), 13.7 (br, B-CH_2), 27.2 ($^3J_{C-P}$ = 51.0 Hz, C=CCH_2), 126.4 (s, =C(B)), 128.2 (*s,* Ar), 128.3, (d, J_{P-C} = 4.08 Hz, Ar), 128.5 (d, $^3J_{C-P}$ = 8.67 Hz, PAr), 130.0 (d, $^4J_{C-P}$ = 2.24 Hz, PAr), 131.3 (d, $^1J_{C-P}$ = 17.2 Hz, *P*Ar), 132.9 (d, J_{C-P} = 10.86 Hz, PAr) 136.75 (br), 196.5 (br. PC=C). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P 9.8 (PPh_2). ^{11}B{^{1}H} NMR ($CDCl_3$): δ_B 13.2 (BEt_2). Elem. Anal.: Calcd for $C_{26}H_{30}BP$: C, 81.26 %; H, 7.87 %. Found; C, 81.16 %; H, 7.78 %.

Synthesis of $Fu_2PCH{=}CH_2$ (4): To a thf solution (12 cm^3) of Bis-(2-furyl)phosphane chloride (Fu_2PCl; 6.96 g, 43.72 mmol) at −78 °C was added dropwise, over 40 minutes, vinyl magnesium bromide (34.75 cm^3, 1.0 M in THF, 34.75 mmol). The resulting mixture was allowed to warm to ambient temperature and then stirred under an argon atmosphere for 24 h., whereupon the solvent was removed under reduced pressure. The mixture was extracted with hexane (30 cm^3), filtered, and the filtrate taken to dryness under reduced pressure to afford **4** as a pale yellow oil. Yield: 5.39 g, 80/8 %. ^{1}H NMR ($CDCl_3$): δ_H 5.66 (ddd, J_{HH} = 18.0, 1.0 Hz, J_{PH} 15.0 Hz, 1 H, PCH=CH_2), 5.86 (ddd, J_{HH} = 11.6 Hz, 1.0 Hz, J_{PH} = 33.7 Hz, 1H, PCH=CH_2), 6.41 (m, 2H, Fu-H^3), 6.67 (ddd, J_{HH} = 18.0, 11.6 Hz, J_{PH} 15.0 Hz, 1H, PCH=CH_2), 6.77 (m, 2H, Fu-H^4), 7.65 (m, 2H, Fu-H^5). ^{13}C NMR ($CDCl_3$): δ_C 110.8 (dd, J = 6.0, 3.0 Hz, Fu-C^3), 120.6 (d, $^3J_{CP}$ = 24.6 Hz, Fu-C^4), 128.9 (d, $^2J_{CP}$ = 23.6 Hz, PCH=CH_2), 132.8 (dd, J = 2.8, 1.5 Hz, PCH=CH_2), 147.3 (m, Fu-C^5), 150.5 (d, $^1J_{CP}$ = 11.1 Hz, Fu-C^2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P −57.05 (s). Elem. Anal.: Calcd for $C_{10}H_9O_2P$: C, 62.46 %; H, 4.72 %. Found; C, 62.41 %; H, 4.80 %.

Synthesis of $Fu_2PCH_2CH_2B(C_8H_{14})$ (5): A solution of **4** (5.18 g, 26.96 mmol) in toluene (20 cm^3) was added to a suspension of 9-BBN dimer (3.29 g, 13.49 mmol) in toluene (60 cm^3) at ambient temperature. The mixture was then heated to 60 °C under an argon atmosphere for 5 h. After cooling to ambient temperature, the solvent was removed under reduced pressure to afford **5** as a white solid, which was washed with hexane (5 cm^5 x 3) and dried in vacuo. Yield: 8.00 g, 94/4 %. ^{1}H NMR ($CDCl_3$): δ_H 1.20 (m, 2H 9-BBN-CH_2), 1.42 (dt, J = 14.2, 7.9 Hz, 2H, CH_2B), 1.67 (br. m, 4H, 9-BBN-CH_2), 1.71 (br. m, 2H, 9-BBN-CH), 1.84 (m., 6H 9-BBN-CH_2), 2.31 (td, J = 8.0, 1.9 Hz, 2H, CH_2P), 6.39 (m, 2H, Fu-H^3), 6.74 (m, 2H, Fu-H^4), 7.63 (m, 2H, Fu-H^5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 20.2 (br. s, CH_2P), 23.0 (br.s, CH_2B), 23.4 (s, 9-BBN-CH_2), 31.2 (s, 9-BBN-CH), 33.4 (s, 9-BBN-CH_2), 110.6 (d, $^2J_{CP}$ = 4.1 Hz, Fu-C^3), 120.2 (d, $^3J_{CP}$ = 24.0 Hz, Fu-C^4), 146.9 (s, Fu-C^5), 152.3 (d, $^1J_{CP}$ = 18.9 Hz, Fu-C^2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P −56.0. ^{11}B{^{1}H} NMR ($CDCl_3$): δ_B = 87.7. Elem. Anal.: Calcd for $C_{18}H_{24}O_2PB$: C, 68.76 %; H, 7.70 %. Found; C, 68.71 %; H, 7.82 %.

Synthesis of $Ph_2P(CH_2)_nB(C_8H_{14})$ (*n* = *2* 6, *3* 7): Based upon literature procedures.[18,21] To $Ph_2PCH{=}CH_2$ (1.559 g, 7.34 mmol) or $Ph_2PCH_2CH{=}CH_2$ (1.206 g, 5.33 mmol) as solution in thf (ca 10 cm^3) was added 9-BBN dimer (0.6 equiv.) as solution in thf (10 cm^3). The resulting mixture was brought to reflux for 3 h. and then allowed to cool to ambient temperature. The solvent was removed under reduced pressure to afford a white solid, which was dissolved in pentane and filtered. The filtrate was concentrated under reduced pressure, then stored at −20°C for 12 h, resulting in the formation of colourless crystals, which were isolated by filtration and dried in vacuo. Yield: 1.49 g, 75.5 % (**6**) 1.31 g, 80.4 % (**7**).

Data for 6: ^{1}H NMR (CD_2Cl_2): δ_H 1.23 (m, 2H, 9-BBN-CH_2), 1.48 (m, 2H, BCH_2), 1.72 (br., 4H, 9-BBN-CH_2), 1.75 (br., 2H, 9-BBN CH), 1.85 (br. m, 6H 9-BBN-CH_2, 2.23 (m, 2H, PCH_2): 7.33-7.44 (m, 10H). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ_C 22.1 (d, $^1J_{CP}$ = 11.8 Hz, PCH_2), 23.1 (s, CH_2B), 23.2 (s, γ-BBN), 31.1 (s, α-BBN), 33.2 (s, β-BBN), 128.3 (d, $^3J_{CP}$ = 6.6 Hz, *m*-Ph), 128.3 (s, *p*-Ph), 132.7 (d, $^2J_{CP}$ = 17.6 Hz, *o*-Ph), 139.4 (d, $^1J_{CP}$ = 14.9 Hz, *i*-Ph). ^{31}P{^{1}H} NMR δ_P −10.1(s). ^{11}B{^{1}H} NMR: δ_B 88.0 (br, s.). **Data for 7**: ^{1}H NMR (CD_2Cl_2): δ_H 1.05 (br. m, 4H, CH_2B and 9-BBN-CH), 1.40 (br. m, 2H 9-BBN-CH_2), 1.57 (br. m, 4H, 9-BBN-CH_2), 1.66 (br. m, 4H, 9-BBN-CH_2), 1.82 (br. m, 2H, 9-BBN-CH_2), 1.95 (m, 2H, $CH_2CH_2CH_2$), 2.35 (dt, J_{PH} = 17.0 Hz, J_{HH} = 7.3 Hz, 2H, PCH_2), 7.38-7.57 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ_C 24.0 (br s, α-BBN), 24.3 (d, J_{CP} = 17.0 Hz, PCH_2CH_2), 25.0 (s, γ-BBN), 26.7 (br. s, BCH_2), 32.3 (d, J_{CP} = 39.0 Hz, PCH_2), 33.3 (s, β-BBN), 128.6 (d, $^3J_{CP}$ = 8.5 Hz, *m*-Ph), 130.2 (d, $^2J_{CP}$ = 2.3 Hz, *o*-Ph), 132.1 (d, $^1J_{CP}$ = 34.1 Hz, *i*-Ph), 132.7 (d, $^1J_{CP}$ = 9.1 Hz, *o*-Ph). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_P 9.82 (br. s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ_B 0.77 (br s.).

Synthesis of *cis*-[Pt{P(Fu)$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}$_2$Cl$_2$] (8): A solution of **5** (0.71 g, 2.27 mmol) in CH_2Cl_2 (8 cm^3) was added to a suspension of $PtCl_2$ (0.30 g, 1.14 mmol) in CH_2Cl_2 (8 cm^3) and the mixture stirred for 4 days. The mixture was then filtered to remove unreacted $PtCl_2$ and the filtrate taken to dryness under reduced pressure to afford **8** as a white solid, which was washed with hexane and then dried *in vacuo.* Yield: 0.82 g, 80.7 %. ^{1}H NMR ($CDCl_3$): δ_H 1.16 (m, 4H, 9-BBN-CH_2), 1.62 (m, 4H, 9-BBN-CH_2), 1.63 (m, 4H, CH_2B) 1.66 (m, 4H, 9-BBN-CH), 1.79 (m, 6H, 9BBN-CH_2), 1.81(m, 6H, 9-BBN-CH_2), 2.73 (td, J = 10.7, 5.4 Hz, 4H, CH_2P), 6.37 (dd, 4H, Fu-H^3), 6.92 (dd, J = 3.5, 1.3 Hz, 4H, Fu-H^4), 7.48 (d, J = 0.7 Hz, 4H, Fu-H^5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 21.7 (br. CH_2B), 23.3 (s, 9BBN-CH_2), 25.0 (m CH_2P), 31.2 (s, 9-BBN-CH), 33.3 (s, 9-BBN-CH_2), 111.2 (t, J = 3.80 Hz, Fu-C^3), 123.6 (m, Fu-C^4), 142.4 (d, $^1J_{C-P}$ = 89 Hz, Fu-C^2), 147.5 (t, $^1J_{CC}$ = 2.8 Hz, Fu-C^5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P −17.6 (s, $^1J_{PPt}$ = 3686.9 Hz). ^{11}B{^{1}H} NMR ($CDCl_3$): δ_B 86.3. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} = -4425.6 (t, $^1J_{PtP}$ = 3686.9 Hz). Elem. Anal.: Cacld for $C_{36}H_{48}O_4B_2P_2Cl_2Pt$: C, 48.38 %; H, 5.41 %. Found: C, 48.45 %; H, 5.50 %.

Synthesis of *cis/trans*-[Pd{P(Fu)$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}$_2$Cl$_2$] (9): As for the platinum species **8**, a CH_2Cl_2 solutions (8 cm^3) of **5** (0.46 g, 1.48 mmol) was combined with a suspension of $PdCl_2$ (0.13 g, 0.74 mmol) in CH_2Cl_2 (8 cm^3) and the mixture stirred for 48 h. The solution was filtered, then solvent removed under reduced pressure to afford a yellow powder. Yield: 0.59 g, 49/7 %. Calcd for $C_{36}H_{48}O_4B_2P_2Cl_2Pd$: C, 53.67 %; H, 5.96 %. Found: C, 53.72 %; H, 5.93 %. 3:1 *cis*:*trans* ***Data for cis-9:*** ^{1}H NMR ($CDCl_3$):[38] δ_H 1.18 (m, 4H, 9-BBN-CH_2), 1.61 (m, 4H, CH_2B), 1.65 (m, 8H, BBN-CH_2 and BBN-CH), 1.79 (m, 16H, BBN-CH_2), 2.76 (m, 4H, CH_2P), 6.38 (m, 4H, Fu-H^3), 6.93 (m, 4H, Fu-H^4), 7.50 (m, 4H, Fu-H^5). ^{13}C{^{1}H} NMR ($CDCl_3$):[50] δ_C 22.0 (br., CH_2B), 23.3 (s, 9-BBN-CH_2), 26.8 (dm, $^1J_{C-P}$ = 38.2 Hz, CH_2P), 31.2 (s, 9-BBN-CH), 33.3 (s, 9-BBN-CH_2), 111.4 (m, Fu-C^3), 124.2 (m, Fu-C^4), 143.1 (dd, $^1J_{C-P}$ = 75.3 Hz, $^3J_{C-P}$ = 3.1 Hz, Fu-C^2), 147.8 (m, 2H, Fu-C^5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P 0.9 (s). ^{11}B{^{1}H} NMR ($CDCl_3$): δ_B = 86. 8. ***Data for trans-9:*** ^{1}H NMR ($CDCl_3$):[38] δ_H 1.18 (m, 4H, 9-BBN-CH_2), 1.61 (m, 4H, CH_2B), 1.65 (m, 8H, BBN-CH_2 and BBN-CH), 1.79 (m, 16H, BBN-CH_2), 2.76 (m, 4H, CH_2P), 6.49 (m, 4H, Fu-H^3), 7.31 (dm, J = 3.5, 4H, Fu-H^4), 7.71 (m, 4H, Fu-H^5). ^{13}C{^{1}H} NMR ($CDCl_3$):[50] δ_C 22.0 (br., CH_2B), 23.3 (s, 9-BBN-CH_2), 26.8 (dm, $^1J_{C-P}$ = 38.2 Hz, CH_2P), 31.2 (s, 9-BBN-CH), 33.3 (s, 9-BBN-CH_2), 111.3 (t, $^2J_{C-P}$ = 3.7 Hz, Fu-C^3), 124.9 (t, $^3J_{C-P}$ = 9.8 Hz, Fu-C^4), 143.6 (t, $^1J_{C-P}$ = 33.1 Hz, Fu-C^2), 148.1 (t, $^4J_{C-P}$ = 2.5 Hz, Fu-C^5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P −11.4. ^{11}B{^{1}H} NMR ($CDCl_3$): δ_B 86. 8.

Synthesis of [Rh(η^4-C$_8$H$_{12}$){P(Fu)$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}Cl] (10): A CH_2Cl_2 solution (8 cm^3) of **5** (0.21 g, 0.67 mmol) was added to a stirred solution of

$[Rh(\eta^4\text{-}C_8H_{12})Cl]_2$ (0.16 g, 0.33 mmol) in CH_2Cl_2 (8 cm^3) and the mixture stirred for 1 h. The solvent was removed under reduced pressure to afford **10** as a yellow powder. Yield 0.31 g, 84.6 %. ^1H NMR ($CDCl_3$): δ 1.21 (m, 2H, 9-BBN-C**H**$_2$), 1.68 (m, 4H, 9-BBN-C**H**$_2$), 1.74 (m, 2H, 9-BBN-C**H**) 1.84 (m, 6H, 9-BBN-C**H**$_2$), 1.84 (m, 2H, C**H**$_2$B), 2.01 (m, 2H, C**H**$_2$-COD), 2.08 (m, 2H, C**H**$_2$-COD), 2.40 (m, 4H, C**H**$_2$-COD), 2.64 (dt, J = 8.6, 7.7 Hz, 2H, C**H**$_2$P), 3.46 (m, 2H, C**H**-COD), 5.50 (m, 2H, C**H**-COD), 6.46 (m, 2H, Fu-**H**$_3$), 6.99 (m, 2H, Fu-**H**$_4$), 7.65 (d, $_3J_{H\text{-}H}$ = 0.8 Hz, 2H, Fu-**H**$_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.5 (d, $^1J_{C\text{-}P}$ = 27.9 Hz, **C**H$_2$P), 22.7 (br. m, **C**H$_2$B), 23.2 (s, 9-BBN-**C**H$_2$), 28.7 (s, COD-**C**H$_2$), 31.0 (s, 9-BBN-**C**H), 33.1 (s, 9-BBN-**C**H$_2$), 33.2 (s, COD-**C**H$_2$), 70.5 (d, $^1J_{C\text{-}Rh}$ = 13.3 Hz, COD-**C**H), 105.6 (dd, $^1J_{C\text{-}Rh}$ = 12.9, $^2J_{C\text{-}P}$ = 7.0 Hz, COD-**C**H), 110.7 (d, $^2J_{C\text{-}P}$ = 6.9 Hz, Fu-**C**$_3$), 122.7 (d, $^3J_{C\text{-}P}$ = 16.3 Hz, Fu-**C**$_4$), 145.9 (d, $^1J_{C\text{-}P}$ = 54.2 Hz, Fu-**C**$_2$), 147.3 (d, $^4J_{C\text{-}P}$ = 3.6 Hz, Fu-**C**$_5$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 2.81 (d, $^1J_{P\text{-}Rh}$ = 154.8 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ_B 85.4 (br. s). Elem. Anal.: Cacld for $C_{26}H_{48}O_2BPClRh$: C, 55.49 %; H, 6.81 %. Found: C, 55.52 %; H, 6.34 %.

Synthesis of [Rh(η^4-C$_{8c}$H$_{12}$){PPh$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}Cl] (11): As for **10**, from 0.080 g (0.26 mmol) of **6** and 0.061 g (0.12 mmol) $[Rh(\eta^4\text{-}C_8H_{12})Cl]_2$ in CH_2Cl_2 (15 cm^3). After removal of the solvent under reduced pressure, the resulting yellow solid was washed with pentane (5 cm^3 x 2) and dried in vacuo. Yield 0.064 g, 88.9 %. ^1H NMR (CD_2Cl_2): 1.27 (m, 2H, 9-BBN-C**H**$_2$), 1.66 (m, 2H, C**H**$_2$B), 1.76 (m, 4H, 9-BBN-C**H**$_2$), 1.85, (br. m, 8H, 9-BBN-C**H**$_2$ and 9-BBN-C**H**), 1.91 (m, 2H, COD-C**H**$_2$), 2.05 (m, 2H, COD-C**H**$_2$), 2.36 (m, 4H, COD-C**H**$_2$), 2.63 (m, 2H, PC**H**$_2$), 3.09 (m, 2H, COD-C**H**), 5.39 (m, 2H, COD-C**H**), 7.35-7.62 (m, 10H, Ar-**H**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 22.9 (d, $^1J_{C\text{-}P}$ = 24 Hz, P**C**H$_2$), 23.7 (br.s, B**C**H$_2$), 24.1 (s, 9-BBN **C**H$_2$), 29.3 (s, COD-**C**H$_2$), 31.4 (br.s, 9-BBN-**C**H), 33.5 (d, J_{CP} = 2 Hz COD-**C**H$_2$), 33.9 (s, 9-BBN **C**H$_2$), 70.1 (d, $^2J_{P\text{-}C}$ = 15 Hz, COD-**C**H), 104.5 (m, COD-**C**H), 128. 0 (d, $^3J_{C\text{-}P}$ = 9 Hz, *m*-**Ar**), 129.8 (s, *p*-**Ar**), 133.3 (d, $^2J_{C\text{-}P}$ = 15 Hz, *o*-**Ar**), 133.6 (d, $^1J_{C\text{-}P}$ = 14 Hz, *ipso*-**Ar**). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ_B 81.5 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_P 28.9 (d, $^1J_{P\text{-}Rh}$ = 147 Hz). Elem. Anal.: Cacld for $C_{30}H_{40}BPClRh$: C, 62.04 %; H, 6.94 %. Found: C, 61.76 %; H, 6.74 %.

Synthesis of [Rh(η^4-C$_8$H$_{12}$){PPh$_2$CH$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}Cl] (12): In CH_2Cl_2 solution (20 cm^3), **7** (0.152 g, 0.44 mmol) and $[Rh(\eta^4\text{-}C_8H_{12})Cl]_2$ (0.102 g, 0.21 mmol) were combined and stirred for 18 h. The solvent was removed under reduced pressure and the resulting deep orange solid washed with pentane (5 cm^3 x 2) and dried in vacuo. Yield 0.10 g, 85.2 %. ^1H NMR (CD_2Cl_2): δ_H 1.24 (m, 4H, 9-BBN-C**H** and BC**H**$_2$), 1.59 (m, 2H, 9-BBN-C**H**$_2$), 1.69 (m, 4H, 9-BBN-C**H**$_2$), 1.84 (m, 6H, 9-BBN-C**H**$_2$), 2.03 (m, 2H, COD-C**H**$_2$), 2.11 (m, 2H, COD-C**H**$_2$), 2.17 (br. s., 2H, CH$_2$C**H**$_2$CH$_2$), 2.34 (m, 4H, COD-C**H**$_2$), 2.54 (m, 2H, PC**H**$_2$), 3.03 (m, 2H, COD-C**H**), 5.47 (m 2H, COD-C**H**),7.39-7.64 (m, 10H, Ar-**H**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ_C 16.5 (d, J_{CP} = 17.0 Hz, PCH$_2$**C**H$_2$), 20.7 (s, BBN-**C**H$_2$), 27.5 (br s, BCH$_2$), 29.3 (s COD-**C**H$_2$) 30.2 (d, J_{CP} = 25.0 Hz, P**C**H$_2$), 31.4 (br. S., 9BBN-**C**H), 33.5 (s, BBN-**C**H$_2$), 70.6 (d, $^2J_{P\text{-}C}$ = 13 Hz, COD-**C**H), 105.1 (m, COD-**C**H),128.5 (d, $^3J_{CP}$ = 8.6 Hz, Ph), 130.5 (br. s., Ph), 133.9 (br. Ph), 134.1 (d, $^1J_{CP}$ = 10.6 Hz, Ph). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): 87.3. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 26.1 (d,^{1} $J_{P,Rh}$ = 147 Hz). Elem. Anal.: Cacld for $C_{31}H_{42}BPClRh$: C 62.54 %, H 7.06 %. Found: C 62.45 %, H 6.94 %.

Synthesis of [Rh(CO){P(Fu)$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}$_2$Cl] (13): A solution of **5** (0.026 g, 0.082 mmol) in CH_2Cl_2 (1 cm^3) was added to a solution of $[Rh(CO)_2Cl]_2$ (0.007 g, 0.021 mmol) in CH_2Cl_2 (1 cm^3) and the mixture stirred for 20 h. The solvent was then removed under reduced pressure to afford **13** as an orange solid, which was recrystallised from a saturated CH_2Cl_2 solution. ^1H NMR (CD_2Cl_2): δ_H 1.21 (m, 2H, C**H**$_2$B), 1.67 (m, 2H, BBN-C**H**$_2$), 1.73 (m, 4H, BBN-C**H**$_2$), 1.76 (m, 2H, BBN-C**H**), 1.85 (m, 6H, BBN-C**H**$_2$), 2.79 (m, 2H C**H**$_2$P), 6.51 (m, 2H, Fu-H), 7.15 (d, ($^3J_{P\text{-}H}$=3.19 Hz) 2H, Fu-H), 7.74 (m, 2H, Fu-H). ^{13}C NMR (CD_2Cl_2): δ_C 21.2 (t, $^1J_{C\text{-}P}$ = 17.3 Hz, **C**H$_2$P), 22.8 (br, **C**H$_2$B), 23.8 (s, BBN-**C**H$_2$), 31.8 (br, BBN-**C**H), 33.7 (s, BBN-**C**H$_2$), 111.5 (t, $^1J_{C\text{-}P}$ = 3.7 Hz, Fu-**C**H), 123.6 (t, $^1J_{C\text{-}P}$ = 9.9 Hz, Fu-**C**H), 147.6 (t, $^1J_{C\text{-}P}$ = 2.3 Hz, Fu-**C**), 148.3 (t, $^1J_{C\text{-}P}$ = 2 Hz, Fu-**C**H), 185.8 (br. **C**O). ^{31}P NMR (CD_2Cl_2): δ_P −5.6 (d, $^1J_{Rh\text{-}P}$= 129 Hz.). ^{11}B NMR (CD_2Cl_2): δ_B 85.9. IR: ν_{CO} 1994 cm^{-1}. Elem. Anal.: Cacld for $C_{37}H_{34}O_5B_2P_2ClRh$: C 55.92 %, H 6.09 %. Found: C 55.70 %, H 5.84 %. ***Crystal data for 13:*** $C_{37}H_{48}B_2ClO_5PRh$, M_w=794.74, monoclinic, P21/c (no. 14), a = 11.2781(6), b = 11.8156(7), c = 14.3231(9) Å, α = 90, β = 98.247(5), γ = 90°. V = 1888.92(19) A^3, Z = 2, D_c 1.397 Mg/m^3. μ(Cu-Ka) = 5.427 mm^{-1}, T = 173(2) K, 3517 independent reflections. Full-matrix F^2 refinement R_1 = 0.0473, wR_2 = 0.1621 on 2654 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 142.4 °], 231 parameters. CCDC 1013337

Synthesis of [Rh(CO){PPh$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}$_2$Cl] (14): As for **13** from **6** (0.037 g, 0.11 mmol) and $[Rh(CO)_2Cl]_2$ (0.010 g, 0.026 mmol) in CH_2Cl_2 (1 cm^3), ^1H NMR (CD_2Cl_2): δ_H 1.17 (m, 2H, 9-BBN-C**H**$_2$), 1.66 (m, 4H, 9-BBN-C**H**$_2$), 1.69 (m, 2H, 9-BBN-C**H**), 1.76 (m, 6H, 9-BBN-C**H**$_2$), 1.94 (m, C**H**$_2$B), 2.92 (m, 2H C**H**$_2$P), 7.01-7.09 (m, 6H Ar), 7.87-7.91 (m, 4H, Ar). ^{13}C NMR (C_6D_6): δ_C 22.4 (t, $^1J_{C\text{-}P}$ = 13 Hz, **C**H$_2$P), 23.1 (br, **C**H$_2$B), 23.3 (s, BBN-**C**H$_2$), 30.9 (br, BBN-**C**H), 33.2 (s, BBN-**C**H$_2$), 128.5 (t, $^1J_{C\text{-}P}$ = 5 Hz, Ar), 129.6 (s, Ar), 133.5 (t, J = 6 Hz, Ar), 135.2 (dt, ^{1}J = 20 Hz, 1 Hz, Ar), 188.4 (br. **C**O). ^{31}P NMR (CD_2Cl_2): δ_P 29.0 (d, $^1J_{Rh\text{-}P}$= 127 Hz.). ^{11}B NMR (CD_2Cl_2): δ_B 84.5. IR: ν_{CO} 1966 cm^{-1}. Elem. Anal.: Cacld for $C_{45}H_{56}OB_2P_2ClRh$: C 64.74 %, H 6.76 %. Found: C 64.60 %, H 6.60 %.

Synthesis of [Ir{P(Fu)$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}Cl$_2$Cp*] (15): A solution of **5** (0.13 g, 0.41 mmol) in CH_2Cl_2 (8 cm^3) was added to a solution of $[IrCl_2Cp^*]_2$ (0.16 g, 0.20 mmol) in CH_2Cl_2 (8 cm^3) and the mixture stirred for 4 days. The solvent was removed under reduced pressure and the resulting brown solid washed with hexane and dried in vacuo. Yield: 0.24 g, 82.1 %. ^1H NMR ($CDCl_3$): δ_H 1.10 (m, 2H, 9-BBN-C**H**$_2$), 1.33 (m, 2H, C**H**$_2$B), 1.47 (d, $^3J_{H\text{-}P}$ = 2.3 Hz, 15H, Cp*-C**H**$_3$), 1.56 (m, 4H, 9-BBN-C**H**$_2$), 1.64 (m, 2H, 9-BBN-C**H**), 1.76 (m, 6H, 9-BBN-C**H**$_2$), 2.94 (dt, J = 8.9, 7.9 Hz, 2H, C**H**$_2$P), 6.54 (dd, J = 1.6, 1.3 Hz, 2H, Fu-**H**^{3}), 7.19 (dd, J = 1.8, 1.3 Hz, 2H, Fu-**H**^{4}), 7.72 (dd, $^3J_{H\text{-}H}$ = 0.8 Hz, 2H, Fu-**H**^{5}). $^{13}C\{^1H\}$ NMR ($CDCl_3$,): δ_C 8.19 (s, Cp*-**C**H$_3$), 21.5 (br. s, **C**H$_2$B), 21.8 (d, J_{CP} 33 Hz, **C**H$_2$P), 23.2 (s, 9-BBN-**C**H$_2$), 31.1 (s, 9-BBN-**C**H), 33.3 (s, 9-BBN-**C**H$_2$), 92.7 (s, Cp*-**C**), 111.2 (d, $^2J_{C\text{-}P}$ = 6.9 Hz, Fu-**C**^{3}), 122.9 (d, $^3J_{C\text{-}P}$ = 15.3 Hz, Fu-**C**^{4}), 147.1 (d, $^1J_{C\text{-}P}$ = 73.4 Hz, Fu-**C**^{2}), 147.0 (d, $^4J_{C\text{-}P}$ = 4.6 Hz, Fu-**C**^{5}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P −22.2. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ_B 87.8.

Synthesis of [Ir{PPh$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}Cl$_2$Cp*] (16): As for **15**, from **6** (0.057 g, 0.171 mmol) and $[IrCl_2Cp^*]_2$ (0.063 g, 0.079 mmol) in CH_2Cl_2 (15 cm^3). The mixture was stirred for 24 h. and then the solvent removed under reduced pressure. The resulting orange solid was washed with pentane (5 cm^3 x 3) and then dried in vacuo. ^1H NMR (CD_2Cl_2): δ_H 0.89 (br. s, 2H C**H**$_2$B), 1.12 (m, 2H, 9-BBN-C**H**$_2$), 1.33 (s, 15H, Cp*), 1.50 (m, 6H, 9-BBN-C**H**$_2$), 1.60 (m, 2H, 9-BBN-C**H**), 1.76 (m, 4H, 9-BBN-C**H**$_2$), 2.98 (m, 2H, PC**H**$_2$), 7.48-7.86 (m, 10H, **Ph**). $^{13}C\{^1H\}$ NMR: δ_C 8.5 (s, **Cp***), 22.5 (H$_2$**C**P), 10.1 (br., 9-BBN-**C**H), 15.0 (s, H$_2$**C**B), 28.0 (s, BBN-**C**H$_2$), 34.0 (s, BBN-**C**H$_2$), 127.8 (s, p-**Ar**), 127.9 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, *m*-**Ar**) 130.0 (C-ring), 130.1, 130.4, 130.4, 131.0, 133.9 (d, $^2J_{C\text{-}P}$ = 7.5 Hz, *o*-**Ar**). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ_B 87.0. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_P −0.53 (s). Elem. Anal.: Cacld for $C_{32}H_{43}BCl_2PIr$: C 52.46 %, H 5.92 %. Found: C 52.35 %, H 5.89 %.

Attempted synthesis of [Ir{PPh$_2$CH$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)}Cl$_2$Cp*]: As for **16**, from **7** (0.067 g, 0.192 mmol) and $[IrCl_2Cp^*]_2$ (0.063 g, 0.079 mmol) in CH_2Cl_2 (10 cm^3). Selected spectroscopic data from product mixture. ^1H

NMR ($CDCl_3$): δ_H 1.10-1.76 (br. m, BBN), 1.31 (s, Cp*), 2.75 (m, C**H**$_2$P), 5.54 (br. s, **H**O-BBN), $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P −3.5 (40), −3.2 (65), 9.8 (14, **7**), 36.7(1). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ_B 0.62 (**7**), 58.7 (HO-BBN), 87.8. ***Crystal data for 17:*** $C_{25}H_{32}Cl_2IrP$, M_w=626.57, monoclinic, P21/c (no. 14), a = 8.6420(8), b = 17.5085(10), c = 32.672(3) Å, α = 90, β = 95.990(3), γ = 90°. V = 4916.6 (7) A^3, Z = 8, D_c 1.693 Mg/m^3. μ(Mo-Ka) = 5.723 mm^{-1}. T = 173(2) K, 10459 independent reflections. Full-matrix F^2 refinement R_1 = 0.0547, wR_2 = 0.1041 on 7033 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 53.8 °], 525 parameters. CCDC 1013338

Supporting Information (see footnote on the first page of this article): Labeled Ortep plots for **1**, **2**, **3**, **13** and **17.**

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[1] For a recent review see: D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46-76.
[2] a) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124-1126; b) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880 – 1881.
[3] a) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050-8053; b) B.-H. Xu, G. Kehr, R. Frohlich, B. Wibbeling, B. Schirmer, S. Grimme, G. Erker, *Angew. Chem. Int. Ed.* **2011**, *50*, 7183-7186; c) G. Erös, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, G. Tárkányi, T. Soös, *Chem. Eur. J.* **2012**, *18*, 574-585; d) J. S. Reddy, B.-H. Xu, T. Mahdi, R. Fröhlich, G. Kehr, D. W. Stephan, G. Erker, *Organometallics* **2012**, *31*, 5638-5649.
[4] C. M. Momming, E. Otten, G. Kehr, R. Frohlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2009**, *48*, 6643-6646.
[5] a) A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem. Int. Ed.* **2009**, *48*, 9839-9843; b) G. Menard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 1796-1797; c) T. Wang, D. W. Stephan, *Chem. Eur. J.* **2014**, *20*, 3036-3039.
[6] E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918-9919; b) E. Theuergarten, T. Bannenberg, M. D. Walter, D. Hoschumacher, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Dalton Trans.* **2014**, *43*, 1651-1662.
[7] B. Birkmann, T. Voss, S. J. Geier, M. Ulrich, G. Kehr, G. Erker, D. W. Stephan, *Organometallics* **2010**, *29*, 5310-5319.
[8] a) A. J. M. Miller, J. E. Bercaw, *Chem. Commun.* **2010**, *46*, 1709-1711; b) C. Appelt, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2013**, *52*, 4256-4259.
[9] For recent reviews see: a) H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924-3957; b) H. Braunschweig, R. D. Dewhurst, *Dalton Trans.* **2011**, *40*, 549-558; c) A. Amgoune, D. Bourissou, *Chem. Commun.* **2011**, *47*, 859; d) G. R. Owen, *Chem. Soc. Rev.* **2012**, *41*, 3535.
[10] a) A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Angew. Chem. Int. Ed.* **1999**, *38*, 2759-2761; b) M. R. St.-J. Foreman, A. F. Hill, G. R. owen, A. J. P. White, D. J. Williams, *Organometallics* **2003**, *22*, 4446-4450.
[11] See for example: a) R. S. Anju, D. K. Roy, B. Mondal, K. Yuvaraj, C. Arivazhagan, K. Saha, B. Varghese, S. Ghosh, *Angew. Chem. Int. Ed.* **2014**, *53*, 2873-2877; b) N. Tsoureas, A. Hamilton, M. F. Haddow, J. N. Harvey, A. G. Orpen, G. R. Owen, *Organometallics* **2013**, *32*, 2840; c) I. R. Crossley, J. Hayes, *J. Organomet. Chem.* **2012**, *716*, 285-288; d) G. Buss, G. Saischek, B. N. Harum, M. Volpe, F. Belaj, N. C. Mösch-Zanetti, *Inorg. Chem.* **2011**, *50*, 12632-12640; e) G. Nuss, G. Saischek, B. N. Harum, M. Volpe, K. Garrerer, G. Belaj, N. C. Mösch-Zanetti, *Inorg. Chem.* **2011**, *50*, 1991-2001; f) G. Dyson, A. Zech, B. W. Rawe, M. F. Haddow, A. Hamilton, G. R. Owen, *Organometallics* **2011**, *30*, 5844-5850; g) M. J. Lopez-Gomez, N. G. Connelly, M. F. Haddow, A. Hamilton, M. Lusi, U. Baisch, A. G. Orpen, *Dalton Trans.* **2011**, *40*, 4647-4659; h) M. J. Lopez-Gomez, N. G. Connelly, M. F. Haddow, A. Hamilton, A. G. Orpen, *Dalton Trans.* **2010**, *39*, 5221-5230; i) I. R. Crossley, A. F. Hill, A. C. Willis, *Organometallics* **2010**, *29*, 326-336 and references therein.
[12] a) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu, D. Bourissou, *Angew. Chem. Int. Ed.* **2006**, *45*, 1611-1614; b) S. Bontemps, G. Buohadir, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2006**, *128*, 12056; c) M. Sircoglou, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron, D Bourissou, *Angew. Chem. Int. Ed.* **2007**, *46*, 8583-8586; d) S. Bontemps, M. Sircoglou, G. Bouhadir, H. Puschmann, J. A. K. Howard, P. W. Dyer, K. Miqueu, D. Bourissou, *Chem. Eur. J.* **2008**, *14*, 731-740; e) S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C. H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *Angew. Chem. Int. Ed.* **2008**, *47*, 1481-1484; f) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C. H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.* **2008**, *130*, 16729-16738.
[13] H. Fong, M.-E. Moret, Y. Lee, J. C. Peters, *Organometallics* **2013**, *32*, 3053-3062.
[14] W. H. Harman, T.-P. Lin, J. C. Peters, *Angew. Chem. Int. Ed.* **2014**, *53*, 1081-1086.
[15] S. N. MacMillan, W. H. Harman, J. C. Peters, *Chem. Sci.* **2014**, *5*, 590.
[16] a) J. Gröbe, R. Martin, *Z. Anorg. Allg. Chem.*. **1992**, *607*, 146-152; b) J. Gröbe, K. Lütke-Brochtrup, B. Krekbs, M. Laege, H. H. Niemeyer, E. U. Wuerthwein, *Z. Naturforsch. B: Chem. Sci.* **2006**, *61*, 882-895.
[17] H. Braunschweig, R. Dirk, B. Ganter, *J. Organomet. Chem.* **1997**, *545-546*, 257-266.
[18] J. Vergnaud, M. Grellier, G. Bouhadir, L. Vendier, S. Sabo-Etienne, D. Bourissou, *Organometallics* **2008**, *27*, 1140-1146.
[19] T. G. Ostapowicz, C. Merkens, M. Hölscher, J. Klankermayer, W. Leitner, *J. Am. Chem. Soc.* **2013**, *135*, 2104-2107.
[20] S. Frömel, G. kehr, R. Fröhlich, C. G. Daniliuc, G. Erker, *Dalton Trans.* **313**, *42*, 14531-14536.
[21] Zwitterionic complexes have also been obtained directly from phosphane-borates such as $[Cy_2P(C_6F_4)BF(C_6F_5)_2]^-$ and $[F_3BC_6H_4PR_2]^-$, and phosphidoborates $[Ph_2PBC_5H_5]^-$ and $[Ph_2PBH_3]^-$. See for example a) S. L. Granville, G. C. Welch, D. W. Stephan, *Inorg. Chem.*, **2012**, *51*, 4711-4721; b) A. L. Gott, W. E. Piers, J. L. Dutton, R. McDonald, M. Parvez, *Organometallics*, **2011**, *30*, 4236-4249 ; c) Y. Kim, R. F. Jordan, *Organometallics,* **2011**, *30*, 4250-4256; d) D. A. Hoic, W. M. Davis, G. C. Fu, *J. Am. Chem. Soc.*, **1996**, *118*, 8176-8177; e) C. A. Jaska, H. Dorn, A. J. Lough, I. Manners, *Chem – Eur J.*, **2003**, *9*, 271-281.
[22] A. Fischback, P. R. Bazinet, R. Waterman, T. D. Tilley, *Organometallics* **2008**, *27*, 1135-1139.
[23] A. J. M. Miller, J. A. Labinger, J. E. Bercaw, *Organometallics* **2010**, *29*, 4499-4516.
[24] A. J. M. Miller, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2010**, *132*, 3301-3303.
[25] R. Jana, S. Chakroborty, O. Blacque, H. Berke, *Eur. J. Inorg. Chem.* **2013**, 4574-4584.
[26] R. Jana, O. Blacque, Y. Jiang, H. Berke, *Eur. J. Inorg. Chem.* **2013**, 3155-3166.
[27] The ability of a rhodium(I) carbonyl species to support a Rh→B interaction has been documented, alongside the capacity of a weakly associated 'Rh→B' unit to activate a thiocarbonyl moiety within the metal coordination sphere, see: I. R. Crossley, A. F. Hill, A. C. Willis, *Organometallics* **2007**, *26*, 3891-3895.
[28] P. Binger, R. Köster, *J. Organomet. Chem.* **1974**, *73*, 205-210.
[29] A. S. Balueva, O. A. Erastov, *Russ. Chem. Bull.* **1988**, *37*, 151-153.
[30] A. S. Balueva, G. N. Nikonov, *Russ. Chem. Bull.* **1993**, *42*, 341-343.
[31] Gröbe[16b] has previously described **2**, attributing a $^{31}P\{^1H\}$ NMR shift of −15.6 ppm as being consistent with the adoption of a P→B interaction. In view of the lack of supporting ^{11}B NMR data in that case, alongside prevailing trends in literature and the present work, we suggest that Gröbe's synthesis likely afforded instead the *'trans'* isomer, devoid of any P→B interaction.
[32] C. E. Anderson, D. C. Apperley, A. S. Batsanov, P. W. Dyer, J. A. K. Howard, *Dalton Trans.* **2006**, 4134.
[33] S. O. Grim, R. P. Molenda, *J. Org. Chem.* **1980**, *45*, 250-252.
[34] T. L. Breen, D. W. Stephan, *Organometallics* **1997**, *16*, 365-369.
[35] Search of the CCDC: F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380.
[36] H. Schmidbaur, M. Sigl, A. Schier, *Oganometallics* **1996**, *529*, 323-327.
[37] a) S. O. Grim, R. L. Kelter, *Inorg. Chim. Acta* **1970**, *4*, 56-60; b) J. A. Rahn, M. S. Holt, M. O'Neil-Johnson, J. H. Nelson, *Inorg. Chem.* **1988**, *27*, 1316-1320; c) X. L. R. Fontaine, D. P. Markham, B. L. Shaw, *J. Organomet. Chem.* **1990**, *291*, 123-129.

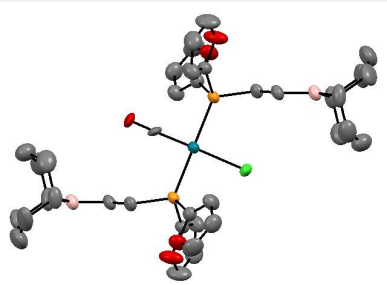
[38] Resonances associated with the bora-organyl fragments show inadequate variation of chemical shift to allow for resolution between the two isomers. A single set of broad multplets is thus apparent in the ^{1}H NMR spectrum, which integrate with internal consistency, and against the furanyl fragments when scaled for the 3:1 isomeric distribution.
[39] It is notable that for both *cis*-**8** and *cis*-**9** unexpected complexity is apparent in the ^{1}H and ^{13}C{^{1}H} NMR data for the furanyl fragments, the resonances appearing as higher-order patterns with additional P–C coupling interactions. Though not elaborated upon, a similar situation has previously been encountered for $[Pd(PFu_3)_2Cl_2]$,[40] one of very few complexes to incorporate a 2-furanylphosphane moiety. Given the absence of such complexity for the *trans* complexes, we reason it must originate with a through-space scalar interaction between the *cis*-disposed phosphane ligands, mediated by the furanyl oxygen-centred lone-pair.
[40] C. M. Hettrick, W. J. Scott, *J. Am. Chem. Soc.* **1991**, *113*, 4903-4910.
[41] M. Bressan, A. Morvillo, J. M. Brown, *J. Organomet. Chem.* **1989**, *361*, 249-254.
[42] S. Serron, S. P. Nolan, K. G. Moloy, *Organometallics* **1996**, *15*, 4301-4306.
[43] K. Wang, M. E. Goldman, T. J. Emge, A. S. Goldman, *J. Organomet. Chem.* **1996**, *518*, 55-68.
[44] S. J. Coles, P. Faulds, M. B. Hursthouse, D. G. Kelly, G. C. Ranger, A. J. Toner, N. M. Walker, *J. Organomet. Chem.* **1999**, *586*, 234-240.
[45] G. W. Kramer, H. C. Brown, *J. Organomet. Chem.* **1977**, *132*, 9-27.
[46] Compounds **2**,[30] **6**[18] and **7**[36] have been previously described in the literature with bulk analysis, and were thus adequately identified from key spectroscopic data; we provide more comprehensive spectroscopic data than have previously been reported. Compound **15**, which is spectroscopically pure (>99%) suffers from the persistence of trace amounts (~0.2 % by NMR integration of Cp*) of $[Cp^*IrCl_2]_2$; this is adequate to prevent obtaining acceptable microanalytical data. As described in the text, compound **17** was obtained as fortuitously isolated crystals, which were not available in adequate quantity to obtain full spectroscopic or analytical data for the pure material.
[47] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.
[48] L. Farrugia, *J. Appl. Cyrstalogr.* **1999**, *32*, 837-838.
[49] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
[50] As with the ^{1}H NMR spectra[38], the 9-BBN fragments and ethyl bridges of *cis* and *trans*-**9** cannot be distinguished between in ^{13}C{^{1}H} or ^{11}B{^{1}H} NMR spectra, but are apparent as broadened resonances, in the former case correlating (HSQC, HMBC) with the respective proton resonances.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

Key Topic

The synthesis and characterisation of a range of singly-bridged phosphine-boranes is described. Their coordination complexes with co-ordinately unsaturated platinum group metals demonstrate a propensity for adopting structures with pendant borane moieties occupying distal positions.



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Synthesis, Structures and Coordination Chemistry of Singly-Bridged Phosphine-Boranes with Coordinately Unsaturated Platinum Group Metals

Keywords: Boranes / Phosphane Ligands / Lewis Acids / Ambiphilic Ligands / Lewis Bases